Mesoscopic non-equilibrium thermodynamics and selected applications

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Abstract: Mesoscopic Non-equilibrium Thermodynamics (MNET) is a theory characterized by the inclusion of a probability density as a thermodynamic variable in the description of a system far from equilibrium. This theory applies to time and length scales which are neither microscopic nor macroscopic. Thus, in these intermediated scales a wide variety of systems (non-aged systems) are properly described. MNET is based on the Gibbs-entropy functional postulate and the conservation of probability. This fact enables us to describe the dynamics of the system in terms of Fokker-Planck equations. As an application, the negative viscosity effect in ferrofluids is analyzed.

I. INTRODUCTION

Equilibrium thermodynamics offers us the theoretical framework to understand the processes of matter and energy exchange between macroscopic systems in equilibrium (aged systems). The majority of ordinary phenomena, such as transport phenomena, correspond to situations in which the conditions of thermodynamic equilibrium do not exist. This is the most serious limitation of equilibrium thermodynamics, since it can only describe phenomena in which the system is always in states of thermodynamic equilibrium (the so-called reversible processes). However, even in situations where the system is out of equilibrium, the concepts and tools provided by equilibrium thermodynamics can be extrapolated.

In order to make this jump, the hypothesis of local equilibrium is introduced [1]. This hypothesis enables us to establish the thermodynamic equilibrium in each of the parts in which we can divide the system, even if the global system is out of equilibrium. Therefore the Gibbs equation, the fundamental thermodynamics equation, is locally valid in each volume element of the system. In this way it is possible to construct a theory that allows us to describe the behavior of macroscopic systems in non-equilibrium situations, the so-called thermodynamic of irreversible processes (TIP).

In the TIP framework we are able to explain in a systematic and rigorous way a great variety of non-equilibrium situations such as diffusion, heat conduction or relaxation phenomena. However, this theory also has a limited range of applicability. In the first place, it will only be valid as long as the hypothesis of local equilibrium is valid. Secondly, as explained in section 2, TIP is an intrinsically linear theory and therefore, it only applies to those phenomena in which the thermodynamic flows are linear functions of the generalized thermodynamic forces, that is, the gradients of thermodynamic state variables. The last condition implies that the system is in a state close to equilibrium and therefore, the fluctuations of the state variables are not very large.

However, when the characteristic time or length scales of the system decreases, Onsager's proposal ceases to be valid for describing these systems. In the mesoscopic level where the fluctuations of the thermodynamic variables can be large, we should resort to a probabilistic treatment of the thermodynamic variables. P. Mazur, in the nineties, formally developed what is now known as mesoscopic non-equilibrium thermodynamics (MNET) [3]. The two essential features that characterize the theory are: the probability density can be taken as the conjugate variable of the chemical potential and, second, the linear equations of non-equilibrium thermodynamics are assumed valid at the mesoscopic level. The methodology of the MNET consists of using the second law of thermodynamics in its local formulation to obtain Fokker-Planck equations for the probability distribution. Once the probability distribution of the system is known, we can obtain all the thermodynamic information of the system. Therefore, MNET is a very flexible theory with a wide range of applicability [2].

The structure of this work will be the following: in section 2 I will present the mathematical formulation of linear irreversible thermodynamics, in section 3 I will show how to obtain Fokker-Planck-type equations from the principles of thermodynamics. Finally, in section 4 I will show how MNET is applied to describe physical phenomena of interest.

II. LINEAR NON-EQUILIBRIUM THERMODYNAMICS

The entropy variation of a system can be written as the sum of two terms

$$dS = dS_e + dS_i \tag{1}$$

where dS_e corresponds to the entropy exchange between the system and the surroundings and dS_i is the entropy production due to irreversible processes occurring inside the system. The second law of thermodynamics states that the entropy production due to irreversible processes

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is positive $dS_i \geq 0$, being zero when the process is reversible. Furthermore, this second principle in its local formulation can be derived from Eq. (1), establishing a balance equation for entropy. So, this principle states that the rate of entropy production density in an irreversible process is positive [4].

$$\sigma = \frac{ds_i}{dt} \geq 0 \tag{2}$$

In addition, for a great variety of phenomena σ can be calculated as the sum of the products of the thermodynamic flows by the conjugated generalized forces, obtaining the following relation:

$$\sigma = \sum_j X_j J_j \tag{3}$$

Where the sum in j involves all the irreversible processes that occur. Besides, when the thermodynamic equilibrium is reached, the flows and the thermodynamic forces vanishes, so the entropy production is zero, as the second principle affirms.

Now we are in position to introduce the most important hypothesis of TIP: thermodynamics fluxes are assumed to be linear functions of the thermodynamics forces (as Hook's law of elasticity, for example):

$$J_i = \sum_j L_{ij} X_j \tag{4}$$

The quantities L_{ij} are called the phenomenological coefficients and Eq. (4) is referred to as the phenomenological equation. This linear relationship is introduced *ad hoc*. The validity of Eq. (4) is justified by experimental evidence. There is a great variety of phenomena in which this expression is fulfilled. For example, the Fourier law expresses that heat flow is proportional to the existing temperature gradient; or on the other hand, Fick's law establishes a linear relationship between the particles flow in a diffusion process and the concentration gradient.

Even, Eq. (4) offers the theoretical framework to study cross-effects phenomena such as thermoelectric current or thermodiffusion. In general, these linear phenomenological relationships are valid when the system is close to equilibrium. However, there may be phenomena in which the linear relationship can have a very wide range of validity, such as Ohm's law, which relates the electric current to the electric potential gradient.

Substituting the value of J, given in Eq. (4), in Eq. (3) we obtain:

$$\sigma = \sum_{i,j} L_{ij} X_i X_j \geq 0 \tag{5}$$

$\sigma \geq 0$ has been imposed according to the second principle of thermodynamics. In order to satisfy the inequality, a series of conditions must be met for the phenomenological coefficients (the matrix $\{L_{ij}\}$ must be positive definite):

$$L_{ii} \geq 0 \tag{6}$$

$$L_{ii} L_{jj} \geq \frac{1}{4}(L_{ij} + L_{ji})^2 \tag{7}$$

On the other hand, to have a knowledge of the $\{L_{ij}\}$ matrix, Onsager obtained the symmetry relations between the phenomenological coefficients for which he obtained the Nobel price. From a microscopic point of view, he studied the time reversal invariance of the equations of individual motion. Thus, he obtained that if the processes being coupled have the same temporal parity then $L_{ij} = L_{ji}$; on the other hand, if they have different parity $L_{ij} = -L_{ji}$. These are the well-known *Onsager's relationships*.

Finally, we can realize as to how TIP has a specific applicability framework beyond which is not possible to describe phenomena far from equilibrium where phenomenological equations can no longer be linearized, as in the case of nonlinear transport phenomena or activated processes, for example. In the next section we will show a theory that can address these problems.

III. MESOSCOPIC THERMODYNAMICS AND STOCHASTIC DYNAMIC

Reducing the characteristic length and time scales of the system entails the necessity of introducing more thermodynamic degrees of freedom. The state of the system (non-aged system) at these scales, the mesoscopic level, is determined by the probability density, $P(\gamma, t)$. Where γ plays the role of an order parameter, a vector which contains the set of all microscopic degrees of freedom, $\gamma \equiv \{\gamma_i\}$. Thus, γ accounts for positions, velocities, orientations, etc.

The evolution of the probability distribution of the system in the γ-space is governed by the continuity equation:

$$\frac{\partial P(\gamma, t)}{\partial t} = -\frac{\partial J}{\partial \gamma} \tag{8}$$

where J is the probability current . This equation establishes the conservation of probability in γ-space. In this theoretical framework, the objective is to deduce the explicit expressions of the probability current through the calculation of the entropy production. The connection between statistical mechanics and thermodynamics is established through the postulate of Gibbs entropy, which connects the thermodynamics with the mesoscopic description in terms of the probability distribution [5].

The Gibbs entropy postulate states that

$$S = S_{eq} - k_B \int_\Gamma P(\gamma, t) \ln \frac{P(\gamma, t)}{P_{eq}(\gamma, t)} d\gamma \tag{9}$$

where the integral extends to the entire γ-space, Γ. To obtain the Fokker-Planck equation, I will proceed as in Ref. [2]. In this sense, assuming that linear non-equilibrium thermodynamics is valid in a γ-space, the equations presented in Section II can be used.

By taking temporal derivatives in Eq. (9), we achieve

$$\frac{\partial S(t)}{\partial t} = \frac{\partial S_{eq}(t)}{\partial t} - k_B \int \ln \frac{P}{P_{eq}} \frac{\partial P}{\partial t} d\gamma \tag{10}$$

Where the normalization condition for $P(\gamma, t)$ and the stationarity of the equilibrium probability distribution has been used. Substituting Eq. (8) into Eq. (10) and using the definition of the non-equilibrium chemical potential we obtain the rate of the entropy production:

$$\sigma(t) = -\frac{1}{T} \int J(\gamma, t) \frac{\partial \mu(\gamma, t)}{\partial \gamma} d\gamma \tag{11}$$

Here, it has been taken into consideration that the probability current vanishes at the borders of the integration area. Moreover, the non-equilibrium chemical potential is given by (see [6] for more details)

$$\mu = k_B T \ln \frac{P}{P_{eq}} + \mu_{eq} \tag{12}$$

It is important to notice that Eq. (11) has the same structure than Eq. (3) although Eq. (3) is local in physical space. Hence, we can realize that the rate of the entropy production density is given by

$$\sigma(\gamma, t) = J(\gamma, t) \left(\frac{-1}{T} \frac{\partial \mu(\gamma, t)}{\partial \gamma} \right) \tag{13}$$

According to TIP the second term on the right hand side of this equation must be the *mesoscopic thermodynamic force* conjugated with the probability current. The link between J and the thermodynamic force is related to a characteristic of MNET mentioned in the introduction: the probability distribution is the conjugate variable of the chemical potential.

Establishing the phenomenological relation between J and the *mesoscopic thermodynamic force* and using Eq. (12) we can obtain the expression of the probability current in terms of the probability distribution:

$$J = -L(\gamma) k_B T \left[P \frac{\partial}{\partial \gamma} \ln P_{eq} + \frac{\partial P}{\partial \gamma} \right] \tag{14}$$

where $L(\gamma)$ is the phenomenological coefficient which can be a function of the state variables. Finally, substituting the expression of the probability current in Eq. (8), we achieve

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \gamma} \left[L(\gamma) k_B T \left(P \frac{\partial}{\partial \gamma} \ln P_{eq} + \frac{\partial P}{\partial \gamma} \right) \right] \tag{15}$$

which is a Fokker-Planck equation for the probability distribution. The Fokker-Planck equation describes the temporal evolution of the probability density whose variables are stochastic. In this way, the Fokker-Planck equation gives us the information about the dynamics of the system if the thermodynamic description of this system is given in terms of the probability distribution, $P(\gamma, t)$ [6].

IV. SELECTED APPLICATIONS

When the dynamics of the system is given by Fokker-Planck equations, MNET can give us a satisfactory description of the phenomenon under study.

In the last years, MNET enabled us to study the energy extraction of non-equilibrium fluctuations. According to this goal, many people have proposed new mechanisms for energy transduction in non-equilibrium systems when they are subjected to the action of a weak periodic force. Thus, the coupling between the external driving and the non-equilibrium fluctuations cause a decrease of the dissipated energy [11]. This phenomenon will be discussed in detail for the particular case of ferrofluids.

A. A mesoscopic approach to the negative viscosity effect in ferrofluids [8]

In the case of a constant field, the viscosity of a ferrofluid is a monotonous function of the magnetic field. However, when the applied field oscillates the behavior of the viscosity is modified. If the frequency of the magnetic field is larger than the local vorticity, the contribution of the oscillating field to the ferrofluid viscosity may be negative. This fact was observed experimentally by J.C. Bacri, R. Perzynski, M.I. Shiliomis and G.I. Burde [7]. They observed how the energy of the magnetic field is transformed into kinetic energy of suspended magnetic particles. This manifests in itself in a decrease of the total viscosity: Its rotational part becomes negative. This is what is known as the *negative viscosity effect* in ferrofluids.

The purpose of this subsection is to show as to how the MNET can explain this effect.This work was made in 1999 by A. Pérez-Madrid. The starting point is to present a Fokker-Planck equation describing the evolution of the probability distribution for the orientation of the dipolar moment of the magnetic particle. After that, the dissipated power and viscosity will be obtained through non-equilibrium thermodynamics [8]. Showing all the mathematical details is not my contention here, but how to approach the problem within the theoretical framework of the MNET

Let us consider a suspension of ferromagnetic spherical particles with a magnetic moment given by $\vec{m} = m_0 \hat{R}$, where $\hat{R}$ is an unit vector accounting for the orientation of the magnetic moment. In addition, there is an applied oscillating magnetic field of the following type, $\vec{H} = He^{-i\omega t}\hat{x}$, where $\hat{x}$ is the unit vector along the x-axis. Moreover, each magnetic particle is under a vortex flow with vorticity, $\vec{\Omega} = 2\omega_0 \hat{z}$. Under these conditions the equation that governs the evolution of $\hat{R}$ is:

$$\frac{d\hat{R}}{dt} = \{\omega_0 \hat{z} + \lambda(t)(\hat{R} \times \hat{x})\} \times \hat{R} \tag{16}$$

where $\lambda(t) = (m_0 H/\xi_r)e^{-i\omega t}$, with ξ_r being the rotational friction coefficient, which depends on the radius

of the particles (a) and the fluid viscosity (η_0). To obtain Eq. (16), the balance between hydrodynamic and magnetic torques have been imposed.

If we treat the orientation of the magnetic moment as a stochastic variable, we must introduce the probability distribution associated with the orientations of $\hat{R}$, $\psi(\hat{R},t)$, whose temporal evolution is given by the Fokker-Planck equation associated with Eq. (16):

$$\frac{\partial\psi(\hat{R},t)}{\partial t} = (\mathcal{L}_0 + \lambda(t)\mathcal{L}_1)\psi(\hat{R},t) \tag{17}$$

where $\mathcal{L}_0$ and $\mathcal{L}_1$ are operators defined by

$$\mathcal{L}_0 = -\omega_0\hat{z}\cdot\mathcal{R} + D_r\mathcal{R}^2 \tag{18a}$$

$$\mathcal{L}_1 = 2\mathcal{R}\cdot\hat{x} - (\hat{R}\times\hat{x})\cdot\mathcal{R} \tag{18b}$$

The rotational $\mathcal{R}$ operator is given in terms of $\hat{R}$ as $\mathcal{R} = \hat{R}\times\partial/\partial\hat{R}$ and $D_r = k_BT/\xi_r$ is the rotational diffusion coefficient. The method to obtain the stochastic dynamics from the deterministic dynamics is shown in Ref. [9], although in this last situation the ferromagnetic particles are in a solid matrix.

In Ref. [8], λ is assumed to be a constant and constitutes a small perturbation. Thus, the Fokker-Planck equation can be solved perturbatively. The response of the system to the perturbation will be calculated using linear response theory. Up to first order in λ the solution of Eq. (17) is

$$\psi(\hat{R},t) = e^{(t-t_0)}\psi^0(t_0) + \int_{t_0}^{t}\lambda(t')e^{(t-t')\mathcal{L}_0}\psi^0(t')dt' \tag{19}$$

This solution contains two different terms: the zero-order solution and the first-order correction, $\psi(\hat{R},t) = \psi^0(\hat{R},t) + \Delta\psi(\hat{R},t)$. With ψ_0 corresponding to the stationary state solution of Eq. (17) in the absence of the external force [10].

Note that the spherical harmonics are the eigenfunctions of the operators $\mathcal{R}_z$ and $\mathcal{R}^2$. In addition, the set of spherical harmonics constitutes a basis in the Hilbert space of the integrable functions over the unit sphere. Hence, we can express the probability distribution in terms of the spherical harmonics. In this way, Eq. (19) is transformed in

$$\psi(\hat{R},t) = \frac{1}{4\pi}\left(1 + \int_{-\infty}^{t} 2\lambda(t')e^{(t-t')\mathcal{L}_0}(\hat{R}\cdot\hat{x})dt'\right) \tag{20}$$

where the zero-order solution is the uniform distribution, $\psi^0 = 1/4\pi$, and the lower limit of the integral has been extended to $-\infty$ to analyze the asymptotic behavior.

The contribution of the external perturbation to the averaged orientation $\hat{R}(t)$ is given by

$$\hat{R}(t) = \frac{1}{4\pi}\int d\hat{R}\hat{R}\int_{-\infty}^{t} 2\lambda(t')e^{(t-t')\mathcal{L}_0}(\hat{R}\cdot\hat{x})dt' \tag{21}$$

Here, Eq. (21) can be written in components in terms of the response function:

$$\hat{R}_i(t) = \int_{-\infty}^{t}\lambda(t')\chi_i(t-t')dt' \tag{22a}$$

where

$$\chi_i(\tau) = \frac{1}{4\pi}\int 2d\hat{R}\hat{R}_i e^{\tau\mathcal{L}_0}(\hat{R}\cdot\hat{x}) \tag{22b}$$

and with $\tau \equiv t - t' > 0$. Besides, values of time higher than t do not contribute to the integral appearing in Eq. (22.a), so we can extend it to infinity. This last fact allows us to write the Eq. (22.a) in terms of the *generalized susceptibility*, which is the Fourier transform of $\chi_i(\tau)$:

$$\chi_i(\omega) = \frac{1}{4\pi}\int_{-\infty}^{\infty} e^{i\omega\tau}d\tau\int d\hat{R}\hat{R}_i e^{\tau\mathcal{L}_0}2(\hat{R}\cdot\hat{x}) \tag{23}$$

Thus, in order to know the viscosity of the system, this result will be used later on to calculate the dissipated power.

According to non-equilibrium thermodynamics the entropy production during the relaxation of the magnetization of the system is

$$\sigma = -\frac{1}{T}\left[\frac{d\vec{M}}{dt}\cdot\vec{H} + \vec{\Omega}\cdot(\vec{M}\times\vec{H})\right] = \sigma_D + \sigma_V \tag{24}$$

where $\vec{M} = cm_0\hat{R}$, with c being the concentration of particles. The way to obtain Eq. (24) is shown in Ref. [8]. The entropy production has two terms, the first one accounts for the entropy production from Debye relaxation (σ_D), whereas the second is related to the viscous dissipation (σ_V). On the other hand, the power dissipated during a period of the field is computed as

$$P(\omega) = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} T\sigma dt \tag{25}$$

If we compute the last integral for the Debye relaxation and the viscous dissipation terms, respectively, we obtain:

$$P_D(\omega) = 6\eta_0\phi\omega\overline{\lambda(t)^2}\,\mathrm{Im}\,\chi_x(\omega) \tag{26a}$$

$$P_V(\omega) = 6\eta_0\phi\omega\overline{\lambda(t)^2}\,\mathrm{Re}\,\chi_y(\omega) \tag{26b}$$

where $\phi = (4\pi/3)a^3c$ is the volume fraction of particles. Note that the total power dissipated is always positive according to the second principle, despite the fact that one of the two terms may be negative. The most interesting term is P_V because is related to the rotational viscosity coefficient in the following way

$$P_V(\omega) = 4\eta_r\omega_0^2 \tag{27}$$

Finally, using the analytical value of χ_y, which is calculated in Ref. [8], in Eq. (26b), we can achieve the following result

$$\eta_r = \frac{\eta_0 \phi \lambda_0^2}{4\omega_0} \left[\frac{\omega_0 + \omega}{4D_r^2 + (\omega_0 + \omega)^2} + \frac{\omega_0 - \omega}{4D_r^2 + (\omega_0 - \omega)^2} \right] \tag{28}$$

This coefficient includes the contribution of the rotational degrees of freedom of the dipoles to the total viscosity of the ferrofluid. The total viscosity of the ferrofluid is given by $\eta = \eta_f + \eta_r$. Being η_f the intrinsic viscosity of the suspension which is given by Einstein law:

$$\eta_f = \eta_0(1 + 2,5\phi) \tag{29}$$

We can realize how η_r becomes negative when the frequency of the external magnetic field is bigger than the vorticity of the fluid. In fact, when we talk about the negative viscosity effect in ferrofluids, we refer to η_r which becomes negative. However, the total viscosity of the suspension is always positive, although a decrease in its value is observed in this regime.

I want to remark that the validity of the Eq. (24) is guaranteed in situations where the magnetic field is not large. Therefore, for larger values of the magnetic field we have to focus on the Fokker-Planck equation. This approach implies to know the evolution of higher-order moments of the probability distribution.

V. CONCLUSIONS

To conclude, I want to emphasize the three main ideas of this work:

In the first place, we have made a brief summary of the theoretical framework of linear irreversible thermodynamics and its methodology based on establishing phenomenological equations relating currents and thermodynamic forces from the entropy production of the system during its relaxation towards equilibrium. We have emphasized the macroscopic character of this theory and the hypotheses introduced about the linearity of the phenomenological equations. Thus, delimiting its range of applicability to motivate the necessity to go further in order to thermodynamically describe non-aged systems, *i.e.* systems far from equilibrium.

Secondly, in order to deal with mesoscopic phenomena where additional thermodynamic degrees of freedom must be considered, we have to use a probabilistic description of the system through the postulate of the Gibbs entropy functional. Imposing the conservation of the probability in γ-space and using the relations of linear non-equilibrium thermodynamics in this γ-space, we have obtained a Fokker-Planck equation for the evolution of the probability distribution of the system. In this way the MNET enables us to incorporate the arbitrary fluctuations of the thermodynamic variables in its dynamics [2], a fundamental fact which must be emphasized.

Finally, I have shown how the MNET can address a situation of interest: reduction of the energy dissipation in mesoscopic systems. I have focused on the particular case of the negative viscosity effect of a suspension of magnetic particles under the action of an oscillating magnetic field. The mesoscopic approach leads us to pose the problem in terms of a Fokker-Planck equation for the probability distribution of the magnetic moment orientation of the particles, which can be resolved in a perturbative manner.

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[1] I. Prigogine, *Introducción a la termodinámica de procesos irreversibles*, 3rd. ed.

[2] I. Santamaría-Holek, *Termodinámica moderna: teoría de no equilibrio con enfoque multidisciplinario*, 1rd. ed., 2014.

[3] P. Mazur, "Mesoscopic nonequilibrium thermodynamics: Irreversible processes and fluctuations", *Physica A*, vol. 274, p. 491 (1999).

[4] S. R. De Groot, P. Mazur, *Non-equilibrium thermodynamics*, Dover, New York, 1984.

[5] D. Reguera, J.M. Rubí and J.M. Vilar, "The Mesoscopic dynamics of thermodynamic systems". J. Phys. Chem. B, vol. 109, pp. 21502-21515 (2005).

[6] A. Pérez-Madrid, "A model for non-exponential relaxation and aging in dissipative systems", J. Chem. Phys. 122, 214914 (2005).

[7] J.C. Bacri, R. Perzynski, M.I. Shiliomis and G.I. Burde, "Negative-Viscosity Effect in a Magnetic Fluid", Phys. Rev. Lett. 75, 2128 (1995).

[8] A. Pérez-Madrid, T. Alarcón, J.M. Vilar and J.M. Rubí, "A mesoscopic approach to the negative viscosity effect in ferrofluids", *Physica A*, 270, pp. 403-412 (1999).

[9] J.M. Rubí, A. Pérez-Madrid and M.C. Miguel, "Relaxation dynamics in systems of magnetic particles", J.Noncryst. Solids 172-174, pp. 495-500 (1994).

[10] P. Hänggi and H. Thomas, "Stochastic processes: Time evolution, symmetries and linear response", Phys. Rep. 88, 207 (1982).

[11] T. Alarcón, A. Pérez-Madrid and J.M. Rubí, "Energy transduction in periodically driven non-hermitian systems", Phys. Rev. Lett. 85, 19 (2000).